On the origin of the surface magnetic anisotropy in manganese–ferrite nanoparticles

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Abstract

Magnetic resonance has been used to obtain the surface anisotropy in manganese–ferrite nanoparticles from 100 to 250 K. The surface anisotropy data has been successfully explained using a model that includes the single-ion (magneto-crystalline) term plus the magnetoelastic term The single-ion surface-anisotropy contribution has been calculated using the mean-field approximation proposed by Millev and Fänhle [Phys. Rev. B 51 (1995) 2937]. The temperature dependence of the magnetostriction has been included in the description of the magnetoelastic term. We found that the surface-anisotropy changes from negative to positive at a characteristic temperature which is explained by the model proposed in this study. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Magnetic fluids; Nanoparticles; Surface anisotropy

Magnetic fluids (MFs) consist of magnetic nanoparticles dressed with a surface molecular layer and dispersed either in aqueous or non-aqueous media as a stable colloidal suspension [1]. The strong response of concentrated MFs to an applied magnetic field has offered many options of technological applications [2]. Also, magnetic nanoparticles have attracted a lot of attention in recent years due to practical purposes spanning from magnetic recording media to cancer diagnosis [3]. In particular, the surface anisotropy plays a key role in the magnetic properties of nanoparticles [4–10]. Therefore, the understanding of the surface-magnetic anisotropy is of extreme interest not only from the fundamental point of view but also for the engineering of new magnetic materials.

The magnetic properties are strongly influenced when the nanoparticle surface is in close contact with different media [11]. Also, recent experiments have shown that the magnetic anisotropy energy is very sensitive to the nanoparticle size [4,5,7]. The effective magnetic anisotropy of metallic iron nanoparticles has been described in terms of volumetric and surface contributions [4]. In iron nanoparticles the surface anisotropy was claimed to be a result of deviations from the spherical symmetry, while the volumetric anisotropy was comparable to the bulk anisotropy [4]. However, the shape effect is not the only contribution to the surface anisotropy. Surface anisotropy of crystallographic nature can also play a key role in nanosized systems [12]. The surface anisotropy would be caused by symmetry reduction of the spin–orbit coupling (and/or crystal field) at the nanoparticle surface, even for a perfect spherical shape [13]. In this study the temperature dependence of the surface-magnetic anisotropy of spherical manganese–ferrite nanoparticles was investigated both experimentally and theoretically. Two contributions were successfully used to explain the temperature dependence of the surface-magnetic anisotropy, namely, the single-ion contribution and the magnetoelastic contribution. Further, the model used in this study allows one to estimate the residual strain at the nanoparticle surface.

The ionic $MnFe_2O_4$-based MF sample used in this study was chemically synthesized by coprecipitating Mn(II) and Fe(III) ions in alkaline medium, following peptization and passivation of the oxide nanoparticles (mean particle diameter of 6.6 nm) in acid aqueous

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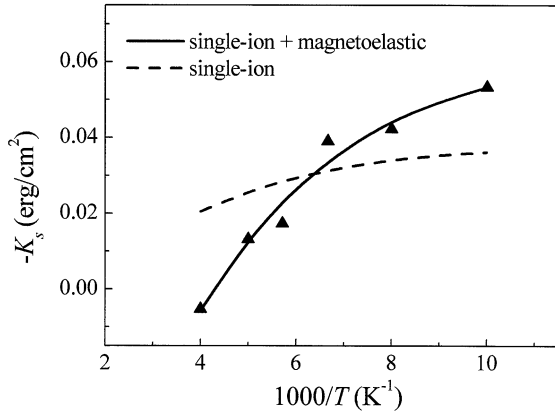*E-mail address:* pcmor@fis.unb.br (P.C. Morais).

Fig. 1. Surface magnetic anisotropy versus $1000/T$ for the 6.6 nm manganese–ferrite nanoparticles. Symbols represent experimental data. The dashed line represents the best fit of the experimental data considering only the single-ion contribution, while the solid line represents the best fit considering the single-ion plus the magnetoelastic contributions.

medium, according to the Massart's method [14]. The particle concentration in the MF sample was fixed at $2 \times 10^{16}\,cm^{-3}$ to reduce particle–particle interaction. The temperature dependence of the effective magnetic anisotropy has been obtained from the magnetic resonance experiments, as discussed in the literature [7,15]. The nanoparticle effective magnetic anisotropy (K_{eff}) is assumed to have two contributions: the volumetric (K_v) and the surface (K_s) anisotropy terms related to one another through $K_{eff} = K_v + (6/D)K_s$, where D is the mean particle diameter [4,7]. Using the magnetic resonance data, the temperature dependence of the saturation magnetization, and the magnetic anisotropy of bulk manganese ferrite [16], the temperature dependence of the surface anisotropy was obtained. Symbols in Fig. 1 represent the surface-magnetic anisotropy values versus $1000/T$. Note that the surface anisotropy values shown in Fig. 1 are in good agreement with the data reported in the literature [4,10]. In addition, note that the surface anisotropy changes from negative to positive at a characteristic temperature. Indeed, the negative (positive) surface anisotropy values in Fig. 1 indicate radial (tangential) orientation of the spins at the nanoparticle surface [6,7].

The single-ion surface anisotropy contribution was calculated using the mean-field approximation proposed by Millev and Fänhle [17]. Under that approximation the reduced magnetization of the nanoparticle (m) has to be calculated. In the calculation of the reduced magnetization of the nanoparticle both Zeeman ($\xi = \mu H/kT$, where μ is the magnetic moment and H is the external field) and magnetic anisotropy ($\sigma = K_{eff}V/kT$, where V is the particle volume) energy terms were taken into

account (it was assumed for simplicity that the anisotropy axis is parallel to the field) to give

$$m = \frac{2\mathrm{i}\sinh(\xi)}{\sqrt{\pi\sigma}}$$
$$\times \frac{\exp(\sigma + \xi^2/4\sigma)}{[\mathrm{erf}[\mathrm{i}\sqrt{\sigma}(1 - \xi/2\sigma)] + \mathrm{erf}[\mathrm{i}\sqrt{\sigma}(1 + \xi/2\sigma)]]}$$
$$- \xi/2\sigma, \tag{1}$$

for $\sigma > 0$ and $\mathrm{erf}(z) = (2/\sqrt{\pi})\int_0^z \exp(-u^2)\,\mathrm{d}u$. The single-ion surface anisotropy (K_s^{SI}) is then given by

$$K_s^{SI} = A\kappa_2(m) + B, \tag{2}$$

where $A = K_s^{SI}$ is the single-ion surface anisotropy at 0 K, B is a constant and $\kappa_2(m)$ is the uniaxial-surface anisotropy coefficient ($0 \leqslant \kappa_2 \leqslant 1$). The mean field approximation proposed by Millev and Fänhle [17] has been used to calculate $\kappa_2(m)$. While A and B are fitting parameters $\kappa_2(m)$ is calculated using Eq. (1). The dashed line in Fig. 1 represents the best fit of the surface anisotropy considering only the single-ion contribution. In contrast, the solid line in Fig. 1 includes the magnetoelastic contribution into the description of the magnetic-surface anisotropy data. The surface anisotropy, considering both contributions (single-ion and magnetoelastic), now reads

$$K_s^{SI+ME} = A\kappa_2(m) + (\tfrac{3}{2}\sigma_{res})\lambda(T) + B, \tag{3}$$

where $\lambda(T)$ and σ_{res} are the magnetostriction and the residual strain, respectively. The temperature dependence of the bulk magnetostriction has been taken from the literature [18]. Notice the good agreement between Eq. (3) and the experimental data. The values obtained from the best curve fitting were $A = 0.14\,erg/cm^2$, $B = 0.12\,erg/cm^2$, and $\sigma_{res} = 0.41\,\text{Å}$. It is important to stress that the values found for $A = 0.14\,erg/cm^2$ times κ_2, in the temperature range of our experiments ($\kappa_2 = 0.99$ at 100 K and $\kappa_2 = 0.73$ at 250 K), give a surface anisotropy contribution ($0.1–1\,erg/cm^2$) in the expected range [19]. Though the contributions to the parameter B are not quite clear at the present time the value found for it also falls in the expected range of the magnetic surface anisotropy ($0.1–1\,erg/cm^2$). The positive single-ion anisotropy parameter (A) indicates that the crystal field favors tangential orientation of the spins at the nanoparticle surface. However, competition between the single-ion term ($A\kappa_2 > 0$) and the magnetoelastic term ($\lambda\sigma_{res} < 0$) leads to a radial to tangential surface spin reorientation at a temperature of about 231 K, similarly to what has been reported for ultrathin magnetic films [20]. The value found for the residual strain corresponds to approximately 5% of the manganese–ferrite lattice constant ($8.50\,\text{Å}$), which is high enough to cause defects on the nanoparticle surface. Magnetic nanoparticles containing different diameter

and/or surface-charged to different amounts (data not shown) have been investigated and their surface-magnetic anisotropy have been successfully explained using the model proposed in this study.

In summary, the surface anisotropy in manganese–ferrite nanoparticles has been investigated as a function of the temperature (100–250 K), using magnetic resonance data. The temperature dependence of the surface anisotropy has been successfully explained in terms of the single-ion and magnetoelastic contributions. While the single-ion surface anisotropy contribution was calculated using the mean-field approximation the temperature dependence of the magnetostriction needs to be considered in the description of the magnetoelastic term.

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